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[Claims]

[Claim 1] A silica meso-structure thin film having a uniaxially oriented pore structure, the thin film being disposed on an arbitrary position of the surface of a high-molecular compound thin film formed on a substrate and being formed into a desired pattern, wherein tubular pores in individual silica meso-structure thin films are oriented uniaxially in the same directions.

[Claim 2] A silica meso-structure thin film according to Claim 1, wherein said high-molecular compound contains two or more continuous methylene groups in its repeat structural unit.

[Claim 3] A meso-porous silica thin film having a uniaxially oriented pore structure, the silica thin film being produced by removing a surfactant contained in pores from the silica meso-structure thin film having a uniaxially oriented pore structure as claimed in Claim 1 or 2.

[Claim 4] A meso-porous silica thin film according to Claim 3, wherein said surfactant is removed by baking or by extraction with an organic solvent.

[Claim 5] A patterning method of a silica meso-structure thin film having a uniaxially oriented pore structure, the method comprising the steps of forming an acid-resistant metal pattern on the surface of a substrate, forming a high-molecular compound thin film on the substrate patterned with the metal, treating the high-molecular compound thin film by rubbing, forming a silica meso-structure thin film on the substrate by holding the

rubbed substrate in an acidic aqueous surfactant solution containing silicon alkoxide and peeling the silica meso-structure formed on the metal pattern of the substrate.

[Claim 6] A patterning method of a silica meso-structure thin film having a uniaxially oriented pore structure, the method comprising the steps of forming an acid-resistant metal pattern on the surface of a substrate, forming a high-molecular compound thin film on the substrate patterned with the metal, treating the high-molecular compound thin film by rubbing, forming a silica meso-structure thin film on the substrate by holding the rubbed substrate in an acidic aqueous surfactant solution containing silicon alkoxide, peeling the silica meso-structure formed on the metal pattern of the substrate and removing the metal pattern formed on the substrate by etching.

[Claim 7] A patterning method of a silica meso-structure thin film according to Claim 5 or 6, wherein said high-molecular compound contains two or more continuous methylene groups in its repeat structural unit.

[Claim 8] A patterning method of a meso-porous silica thin film having a uniaxially oriented pore structure, the method comprising the steps of forming an acid-resistant metal pattern on the surface of a substrate, forming a high-molecular compound thin film on the substrate patterned with the metal, treating the high-molecular compound thin film by rubbing, forming a silica meso-structure thin film on the substrate by holding the rubbed substrate in an acidic aqueous surfactant solution containing silicon alkoxide, peeling the silica meso-structure

formed on the metal pattern of the substrate and removing the surfactant from the silica meso-structure thin film formed on the substrate.

[Claim 9] A patterning method of a meso-porous silica thin film having a uniaxially oriented pore structure, the method comprising the steps of forming an acid-resistant metal pattern on the surface of a substrate, forming a high-molecular compound thin film on the substrate patterned with the metal, treating the high-molecular compound thin film by rubbing, forming a silica meso-structure thin film on the substrate by holding the rubbed substrate in an acidic aqueous surfactant solution containing silicon alkoxide, peeling the silica meso-structure formed on the metal pattern of the substrate, removing the metal pattern formed on the substrate by etching and removing the surfactant from the silica meso-structure thin film formed on the substrate.

[Claim 10] A patterning method of a meso-porous silica thin film according to Claim 8 or 9, wherein said high-molecular compound contains two or more continuous methylene groups in its repeat structural unit.

[Claim 11] A patterning method of a meso-porous silica thin film according to Claim 8 or 9, wherein said surfactant is removed by baking or by extraction with an organic solvent.

[Claim 12] A structure comprising two or more films containing plural pores on a substrate, wherein an organic compound film is interposed between said film and said substrate and pores contained in each of said films are arranged in substantially

parallel to each other.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a silica meso-structure thin film formed by patterning, a meso-porous silica thin film formed by patterning, a patterning method of a silica meso-structure thin film and a patterning method of a meso-porous silica thin film, relates, particularly to the applications of an inorganic oxide porous material to be used for catalysts and adsorbents, and relates more particularly to a silica meso-structure thin film formed by patterning in a desired form on a desired position of the substrate, the thin film being provided with tubular pores oriented in a desired direction under control.

[0002]

[Prior Art] Porous materials are utilized in various fields such as adsorption and separation. According to IUPAC, the porous material is classified into a micropore having a pore diameter of 2 nm or less, meso-pore having a pore diameter of 2 to 50 nm and a macropore having a pore diameter of 50 nm or more. As the microporous material, natural aluminosilicate, zeolite such as synthetic aluminosilicate, metal phosphates and the like are known. These compounds are utilized for selective adsorption, shape selective catalytic reaction and a molecular size reactor by making use of a pore size.

[0003] In the microporous crystals which have been recently

reported, the maximum pore diameter is about 1.5 nm and therefore, a synthesis of a solid having a large size is an important problem to undergo the adsorption and reaction of a compound which is so bulky that a micropore cannot adsorb. As materials having such a large pore, silica gel, pillared clay and the like are known. However, these materials each have a wide distribution of pore diameter, giving rise to the problem concerning the control of pore diameter.

[0004] In such a situation, two different methods for synthesizing meso-porous silica having a structure in which meso-pores regular in sizes are arranged like a honeycomb were developed at the same time. One of materials synthesized using these methods is a material called MCM-41 which is synthesized by the hydrolysis of silicon alkoxide in the presence of a surfactant as described in "Nature", vol. 359, p.710 and the other is a material called FSM-16 synthesized by intercalating an alkylammonium between kanemite layers which are respectively a kind of phyllosilicic acid as described in "Journal of Chemical Society Chemical Communications", vol. 1993, p.680. In both methods, it is considered that an aggregate of surfactants used as a mold to control the structure of silica. These materials are very useful materials as catalysts or adsorbents for bulky molecules which cannot enter into pores of zeolite.

[0005] It is known that meso-porous silica having such a regular pore structure exhibits various macroscopic forms. Examples of these forms include a thin film, fibers, small sphere and monolith. Because these various forms can be controlled,

meso-porous silica is expected to be applied to functional materials such as optical materials and electronic materials besides catalysts and adsorbents.

[0006] When these meso-porous materials having such a regular pore structure are applied to the fields of functional materials other than catalysts, technologies for supporting these materials uniformly on the substrate are important. Examples of the method of forming a uniform meso-porous silica thin film on the substrate include a spin coating method as described in, for example, "Chemical Communications", vol. 1996, p.1149, a dip coating method as described in "Nature", vol. 389, p.364 and a method in which a film is precipitated on the surface of a solid as described in "Nature", vol. 379, p.703.

[0007]

[Problems to be Solved by the Invention] These current methods for producing a meso-porous silica thin film involves the problems as will be described below. Specifically, in the case of the spin coating film or the like, the meso-structure has no orientation over the entire film and therefore, pores cannot be oriented. Also, in the case of the method in which a silica meso-structure is precipitated on the surface of a substrate, the film to be formed largely depends on the substrate, the formation of a film having orientation is limited to the case of using a substrate, such as the cleavage plane of mica or graphite or the (110) plane of a silicon single crystal, which has atomic level orderliness.

[0008] For this reason, the technologies for forming a

meso-porous silica thin film having orientation at an arbitrary position on the substrate have been desired. As the technologies developed to solve this problem, a method using a substrate is proposed, the substrate being provided with a high-molecular compound thin film formed on its surface which is then rubbed as described in "Chemistry of Materials", vol. 11, p.1609.

[0009] Also, in the case of the conventional silica meso-structure thin film, its macroscopic shape is not controlled. In order to apply the silica meso-structure thin film to devices or the like, the formed meso-porous silica thin film having a uniaxially oriented pore structure is formed into an arbitrary shape by patterning on the above arbitrary substrate.

[0010] The present invention has been made in view of the above problems and is to provide a highly continuous and uniform silica meso-structure thin film or a meso-porous silica thin film which has a uniaxially oriented pore structure and is formed into an arbitrary shape on a desired position of an arbitrary substrate by patterning. Also, the present invention is to provide a patterning method of the above silica meso-structure thin film and a patterning method of the above meso-porous silica thin film.

[0011]

[Means for Solving the Problem] According to a first embodiment of the present invention, there is provided a silica meso-structure thin film having a uniaxially oriented pore structure, the thin film being disposed on an arbitrary position

of the surface of a high-molecular compound thin film formed on a substrate and being formed into a desired pattern, wherein tubular pores in individual silica meso-structure thin films are oriented uniaxially in the same directions.

[0012] According to a second embodiment of the present invention, there is provided a meso-porous silica thin film having a uniaxially oriented pore structure, the silica thin film being produced by removing a surfactant contained in pores from the above silica meso-structure thin film having a uniaxially oriented pore structure.

[0013] According to a third embodiment of the present invention, there is provided a patterning method of a silica meso-structure thin film having a uniaxially oriented pore structure, the method including the steps of forming an acid-resistant metal pattern on the surface of a substrate, forming a high-molecular compound thin film on the substrate patterned with the metal, treating the high-molecular compound thin film by rubbing, forming a silica meso-structure thin film on the substrate by holding the rubbed substrate in an acidic aqueous surfactant solution containing silicon alkoxide and peeling the silica meso-structure formed on the metal pattern of the substrate.

[0014] According to a fourth embodiment of the present invention, there is provided a patterning method of a silica meso-structure thin film having a uniaxially oriented pore structure, the method including the steps of forming an acid-resistant metal pattern on the surface of a substrate, forming a high-molecular compound thin film on the substrate patterned with the metal, treating

the high-molecular compound thin film by rubbing, forming a silica meso-structure thin film on the substrate by holding the rubbed substrate in an acidic aqueous surfactant solution containing silicon alkoxide, peeling the silica meso-structure formed on the metal pattern of the substrate and removing the metal pattern formed on the substrate by etching.

[0015] According to a fifth embodiment of the present invention, there is provided a patterning method of a meso-porous silica thin film having a uniaxially oriented pore structure, the method including the steps of forming an acid-resistant metal pattern on the surface of a substrate, forming a high-molecular compound thin film on the substrate patterned with the metal, treating the high-molecular compound thin film by rubbing, forming a silica meso-structure thin film on the substrate by holding the rubbed substrate in an acidic aqueous surfactant solution containing silicon alkoxide, peeling the silica meso-structure formed on the metal pattern of the substrate and removing the surfactant from the silica meso-structure thin film formed on the substrate.

[0016] According to a sixth embodiment of the present invention, there is provided a patterning method of a meso-porous silica thin film having a uniaxially oriented pore structure, the method including the steps of forming an acid-resistant metal pattern on the surface of a substrate, forming a high-molecular compound thin film on the substrate patterned with the metal, treating the high-molecular compound thin film by rubbing, forming a silica meso-structure thin film on the substrate by holding the

rubbed substrate in an acidic aqueous surfactant solution containing silicon alkoxide, peeling the silica meso-structure formed on the metal pattern of the substrate, removing the metal pattern formed on the substrate by etching and removing the surfactant from the silica meso-structure thin film formed on the substrate.

[0017] In the above embodiments, the high-molecular compound contains two or more continuous methylene groups in its repeat structural unit. Also, the above surfactant is preferably removed by baking or by extraction with an organic solvent.

[0018] According to a seventh embodiment of the present invention, there is provided a structure including two or more films containing plural pores on a substrate, wherein an organic compound film is interposed between the film and the substrate and pores contained in each of these films are arranged in substantially parallel to each other.

[0019]

[Preferred Embodiments of the Present Invention] The present invention relates to a silica meso-structure thin film having a uniaxially oriented pore structure, the thin film being disposed on an arbitrary position of the surface of a high-molecular compound thin film formed on a substrate and being formed into a desired pattern, wherein tubular pores in individual silica meso-structure thin films are oriented uniaxially in the same directions. Also, the present invention relates to a meso-porous silica thin film having a uniaxially oriented pore structure, the silica thin film being produced

by removing a surfactant contained in pores from the above silica meso-structure thin film having a uniaxially oriented pore structure.

[0020] In order to remove the surfactant, baking or extraction with a solvent is used. The silica meso-structure thin film of the present invention enables the removal of the surfactant perfectly without impairing the form by baking. Also, when the extraction with a solvent is used, a meso-porous silica thin film can be formed on a substrate using a material which cannot stand to the baking though it is difficult to remove 100% of the solvent. Also, the possibility of the recovery of the used surfactant is one of the advantages of the solvent extraction method.

[0021] The present invention also relates to a patterning method of a silica meso-structure thin film having a uniaxially oriented pore structure, the method involving the steps of forming an acid-resistant metal pattern on the surface of a substrate, forming a high-molecular compound thin film on the substrate patterned with the metal, treating the high-molecular compound thin film by rubbing, forming a silica meso-structure thin film on the substrate by holding the obtained substrate in an acidic aqueous surfactant solution containing silicon alkoxide and peeling the silica meso-structure formed on the metal pattern of the substrate.

[0022] A step of removing the metal pattern formed on the substrate in the fist step by etching is added to this method, thereby making it possible to obtain a pattern only of a silica

meso-structure thin film having a uniaxially oriented pore structure finally.

[0023] In the present invention, a silica meso-structure thin film and a meso-porous silica thin film superior in, particularly, the continuity of the film and the uniaxial orientation of pores can be obtained by using, as the high-molecular compound, one containing two or more continuous methylene groups in the repeat structural unit.

[0024] The present invention will be explained by way of an embodiment. As the reactor to be used in the formation of the silica meso-structure thin film of the present invention, a reactor having, for example, such a structure as shown in Fig. 2 is used. Any material may be used as the material of the reactor without any particular limitation insofar as it is resistant to chemicals and particularly, acids and polypropylenes or Teflon (registered trademark) may be used. A substrate holder 23 made of a material resistant to acids is placed, for example, in the reactor 21 as shown in Fig. 2 and a substrate 25 is held using the substrate holder 23. Fig. 2 shows an example in which the substrate is held horizontally; however, the substrate is not limited to the form horizontally placed.

[0025] Fig. 3 is an explanatory view showing the method of holding the substrate in the reaction solution. Also, a substrate 32 is generally held in a reaction solution 31 as shown in Fig. 3(A). However, the same thin film may be formed also in the case of holding the substrate in such a manner that the surface processed by orientation treatment is made to be in

contact with the surface of the reaction solution as shown in Fig. 3(B). Also, when, as shown in Fig. 3(C), a cover 34 is used through a spacer 33 to protect the surface of the substrate from convection during reaction, the uniformity of a meso-porous silica thin film to be formed tends to be improved. The reactor may be further placed in a closed container made of a highly stiff material such as stainless so as not to be broken by pressure during reaction.

[0026] As the reaction solution in Fig. 3, a solution is used which is obtained by blending an acid such as hydrochloric acid in an aqueous surfactant solution, by adjusting the solution to pH 2 or less which is the isoelectric point and by blending an alkoxide of silicon such as tetraethoxysilane. The surfactant is properly selected from cationic surfactants such as a quaternary alkylammonium and nonionic surfactants such as amphipathic compounds containing an alkylamine or polyethylene oxide as a hydrophilic group. The length of a molecule of the surfactant to be used is determined corresponding to the pore diameter of the intended meso-structure. Also, an additive such as mesitylene may be added to increase the diameter of the surfactant micelle.

[0027] As the substrate, one formed with a pattern of a thin film of a metal having acid resistance such as platinum or gold on the surface thereof is used. Though no particular limitation to the material of the substrate to be used, a material stable in an acidic condition is preferable. Examples of these materials include quartz glass, ceramics, resins or the like

may be used. These metal thin films are respectively formed by a method such as sputtering and the photolithographic method is used to form an arbitrary pattern.

[0028] A high-molecular compound thin film is formed by spin coating or the like on the substrate on which this metal pattern is formed and further, the film is rubbed. The rubbing treatment is usually carried out by rotating a roller with a cloth bound around it in such a manner that the roller is in contact with the surface of the substrate.

[0029] Though no particular limitation is imposed on the high-molecular compound thin film to be formed on the surface insofar as it is not denatured in the reaction condition under which a silica meso-structure thin film is formed. However, a silica meso-structure thin film superior in uniaxial orientation and regularity of a meso-structure is obtained in the case of using a material including two or more continuous methylene groups in the repeat structural unit. When the number of methylene groups in the repeat structural unit is 2 or more and 20 or less, a silica meso-structure thin film having, particularly, good uniaxial orientation is obtained. When the number of methylene groups exceeds the above range, the uniaxial orientation tends to be deteriorated. This reason is considered to be that in the case where the reaction temperature is raised when the silica meso-structure thin film is precipitated as will be described later, the orientation of the polymer which is given by the rubbing is lost.

[0030] A silica meso-structure thin film can be precipitated

on the substrate under this condition. The rate of generation of $SiO_2$ precipitate is small on the acid side and, particularly, in the vicinity of the isoelectric point and such a phenomenon that a precipitate generates instantly after an alkoxide is added does not occur unlike the case of a reaction under a basic condition. There is no particular limitation to the temperature at which the thin film is precipitated and appropriate temperature is selected from a temperature ranging from ambient temperature to about 100°C. The reaction time is several hours to several months.

[0031] The silica meso-structure thin film thus formed on the substrate is washed in pure water to remove excess surfactant and acid. In this step, the silica meso-structure thin film formed on the place where the metal thin film is present as the undercoat is peeled easily from the substrate and only the silica meso-structure thin film precipitated on the place where the metal thin film is not present is left on the substrate. The silica meso-structure on the metal can be peeled more perfectly by carrying out an ultrasonic treatment according to the need. Though the reason why the formed silica meso-structure thin film is easily peeled off on the place where the metal is present as the undercoat is not clarified, it is inferred that a difference in adhesion between the high-molecular compound thin film and the substrate is one of the reasons. A silica meso-structure pattern which is inverse to the metal pattern formed on the undercoat is thus obtained on the substrate.

[0032] In this condition, the metal pattern is formed on the

place where the silica meso-structure thin film is not formed and therefore, a step of removing the metal thin film pattern formed in the first step is necessary to form a pattern of only the silica meso-structure thin film. Because silica is highly resistant to chemicals, the general wet etching method may be applied to this case. In the case of, for example, platinum, the metal thin film is treated with heated aqua regia to form a pattern of only the silica meso-structure thin film.

[0033] A meso-porous silica thin film can be produced by removing template surfactant micelles existing in pores from this silica meso structure thin film. For example, baking or extraction with a solvent is used to remove the surfactant. For example, the silica meso-structure thin film is baked at 550°C in the air for 10 hours, thereby making it possible to remove the surfactant perfectly therefrom with scarcely destroying the meso-structure and uniaxial orientation. Also, if the solvent extraction is used, a meso-porous silica thin film can be formed on a substrate of a material which cannot stand to baking, though it is difficult to remove the surfactant perfectly. Other than these methods, any method may be used insofar as it can remove the surfactant without destroying the meso-structure. The above metal pattern may be removed after removing the surfactant.

[0034] The object of the present invention explained above is firstly to control the orientation of rod-like pores in the silica meso-structure thin film precipitated on the substrate by the orientation regulating force of the high-molecular compound which has been treated by rubbing. The object of the

present invention is secondarily to form a pattern by making use of a difference in the adhesion of the silica meso-structure to the substrate due to a difference in the material of the undercoat of the high-molecular compound thin film treated by rubbing.

[0035]

[Examples] The present invention will be explained in more detail by way of examples, which, however, are not limited to the examples. Also, the materials and reaction conditions may be changed freely to the extent that a silica meso-structure thin film having the same structure is obtained.

[0036] Example 1

This example is one in which a thin film of a polymer having six continuous methylene groups in the principal chain part of the repeat unit is formed on a quartz glass with a platinum thin film pattern formed thereon and then, the thin film is treated by rubbing, and the obtained substrate is used to form a pattern of a silica meso-structure thin film having a uniaxially oriented porous structure.

[0037] Fig. 4 is a schematic view showing the platinum thin film pattern formed on the quartz glass substrate. A platinum thin film 41 was formed and a platinum pattern as shown in Fig. 4 was formed using the photolithographic method. Numeral 42 shows the exposed part of the substrate. The film thickness of platinum was about 100 nm. This substrate was washed with acetone, isopropyl alcohol and pure water to clean the surface in an ozone generator. Then, an NMP solution of a polyamic acid

A which was a precursor was applied to the substrate by spin coating and baked at 200°C for one hour to form a thin film of polyimide A having the following structure.

[0038]

[Chemical Formula 1]

(Polyimide A)

[0039] The entire surface of the substrate was rubbed in one direction in the conditions shown in Table 1 and the obtained substrate was used as the substrate used to precipitate a silica meso-structure thin film. The rubbing direction is shown as the arrow in Fig. 4.

[0040]

[Table 1]

Table 1: Rubbing Condition of Polyimide A

| | |
|---|---|
| Cloth material | Nylon |
| Roller diameter(mm) | 24 |
| Amount of thrust(mm) | 0.4 |
| Rotation (rpm) | 1000 |
| Stage speed (mm/min) | 600 |
| Repeated rotation | 2 |

[0041] Cetyltrimethylammonium chloride of 2.82 g was dissolved in 108 ml of pure water, to which was then added 48.1 ml of 36% hydrochloric acid and the mixture was stirred for 2 hours to prepare an acid solution of a surfactant. Tetraethoxysilane (TEOS) of 1.78 ml was added to this solution and the mixture

was stirred for two minutes and 30 seconds. The resulting mixture was poured into a Teflon (registered trademark) container which had the structure shown in Fig. 2 and contained a substrate holder such that the substrate was held in the solution. The surface of the substrate was coated with a quartz glass cover through a spacer about 0.2 mm in thickness to prevent the convection from adversely affecting the orientation.

[0042] The composition (mol ratio) of the solution was finally as follows: $H_2O$ = 100, HCl = 7, cetyltrimethylammonium chloride: 0.11 and TEOS = 0.10. A lid was put on this container, which was further placed in a closed stainless container and then kept in an oven kept at 80°C. The holding time was set to 48 hours.

[0043] The substrate brought into contact with the reaction solution for a given time was taken out of the container, thoroughly washed with pure water and then subjected to ultrasonic treatment performed in pure water. When the substrate was observed after dried in the air, it was confirmed that the thin film formed on the place where platinum was formed was perfectly peeled off and a transparent thin film was formed only on the part from which quartz glass was exposed.

[0044] Further, this sample was set to an optical microscope to observe the place where the transparent thin film was formed. As a result, as typically shown in Fig. 5, the condition that an ellipsoidal texture 52 was arranged in one direction was observed. As to the direction of the arrangement, the direction of the major axis of the observed ellipsoidal texture was perpendicular to the rubbing direction. Numeral 51 is the silica

meso-structure having a uniaxially oriented pore structure.

[0045] The transparent thin film formed by patterning on this substrate was subjected to X-ray diffraction analysis. As a result, a diffraction peak specific to the (100) plane of a silica meso-structure having a hexagonal structure with a plane spacing of 3.60 nm was confirmed, to find that the transparent thin film had a hexagonal pore structure. Any peak except for the diffraction peak specific to platinum was not observed in a wide-angle area and it was therefore found that silica constituting the wall was amorphous. From this result, it was confirmed that the transparent thin film formed on the substrate was a silica meso-structure thin film having a hexagonal structure.

[0046] The in-plane X-ray diffraction analysis of this silica meso-structure was made to quantitatively evaluate the uniaxial orientation of meso-channels in the silica meso-structure thin film. This method is used to measure the in-plane revolution dependency of X-ray diffraction strength which is originated from the (110) plane perpendicular to the surface of the substrate as described in "Chemistry of Materials", vol. 11, p1609 and the orientation direction and distribution of orientation direction can be examined. As a result of the in-plane diffraction analysis, meso-channels were oriented in a direction perpendicular to the direction of rubbing in the silica meso-structure thin film produced in this example and the distribution of orientation direction showed that the half-value width was about 15°.

[0047] It was confirmed from these results that a silica meso-structure thin film having an arbitrary shape and a uniaxially oriented pore structure was obtained at an arbitrary position of the substrate by the method of the present invention.

[0048] The substrate on which a silica meso-structure thin film having a uniaxially oriented pore structure was placed in a muffle furnace to heat the substrate up to 550°C at a rate of 1°C/min., followed by baking in the air for 10 hours. No difference was observed in the shape of the silica meso-structure thin film before and after the baking. Further, the X-ray diffraction analysis of the substrate with the silica meso-structure formed thereon after the baking was made, with the result that a diffraction peak with a plane spacing of 3.44 nm was observed to confirm that the hexagonal pore structure was retained.

[0049] The presence of any diffraction peak was not confirmed in the wide-angle area even after baking and it was confirmed that silica of the wall remained amorphous. Also, it was confirmed that organic components originated from the surfactant was not left in the baked sample by analysis such as an infrared absorption spectrum. This showed that a meso-porous silica thin film having uniaxially oriented hollow pores could be formed into a desired shape at a desired position on the substrate by the method of the present invention.

[0050] The in-plane X-ray diffraction analysis of the meso-porous silica thin film formed by patterning after baking was also made to investigate the in-plane revolution angle

dependency of (110) plane diffraction strength, to find that the half-value width in the distribution of the direction of orientation was about 15°. It was confirmed from these results that the silica meso-structure kept the uniaxial orientation of the pore structure almost perfectly even after baking.

[0051] The silica meso-structure thin films formed by patterning before and after baking were cut in parallel to the rubbing direction to observe the section by a transmission electron microscope, to confirm that the both had pores having a hexagonal structure. It was confirmed that the meso-pores were oriented along the direction of the major axis of an ellipsoidal texture of the silica meso-structure, that is, in a direction perpendicular to the rubbing direction. Fig. 1 shows a typical view of the section of the silica meso-complex thin film as viewed from the direction perpendicular to the rubbing direction.

[0052] In Fig. 1, numeral 11 represents a silica meso-structure having a uniaxially oriented pore structure, numeral 12 represents a platinum thin film, numeral 13 represents a quartz substrate, numeral represents a polyimide orientation film treated by rubbing, numeral 15 represents a surfactant rod-like micelle or pore and numeral 16 represents silica.

[0053] The adhesion of the mesoporous silica thin film to the substrate was greatly improved by baking. This is considered to be because the undercoat quartz substrate and the meso-porous silica layer form a partial bond by the dehydration condensation of silanol.

[0054] Example 2

This example is an example in which after a pattern of a silica meso-structure thin film is formed in the same method as in Example 1, the metal pattern formed first is removed and further, the surfactant is removed from the pores by solvent extraction.

[0055] The same platinum pattern that was used in Example 1 was formed on a quartz glass substrate by using the photolithographic method. The film thickness of platinum was 100 nm. An NMP solution of polyamic acid A was applied to the substrate formed with this platinum pattern in the same procedures as in Example 1 by spin coating, followed by baking to form a polyimide A thin film.

[0056] The thin film was rubbed in one direction over the entire surface of the substrate in the same procedures as in Example 1 mentioned above and the obtained substrate was used as a substrate for precipitating a silica meso-structure thin film having a uniaxially oriented pore structure.

[0057] Next, a silica meso-structure thin film was precipitated on this substrate in the same procedures as in Example 1 as mentioned above, followed by washing with pure water and ultrasonic treatment in pure water. As mentioned above, the thin film formed on the place where platinum was formed was perfectly peeled off and a transparent silica meso-structure thin film having a uniaxially oriented pore structure was formed on the part from which the quartz glass was exposed among the produced platinum thin film pattern.

[0058] The substrate with the silica meso-structure thin film

pattern which was formed in this manner was immersed in 75°C aqua regia (mixed solution of concentrated hydrochloric acid + concentrated nitric acid ) (3 : 1 by volume) and held in the solution until platinum was completely dissolved. The condition of the substrate formed with the pattern of the silica meso-structure after platinum is removed is shown typically in Fig. 6. Numeral 61 represents a silica meso-structure having a uniaxially oriented pore structure and numeral 62 represents a substrate.

[0059] The pattern only of the silica meso-structure thin film could be formed on the glass substrate by this step. It was confirmed, from the X-ray diffraction analysis of the substrate obtained after platinum was removed, that the treatment using aqua regia had no influence on the pore structure.

[0060] The substrate formed with the pattern of a silica meso-structure thin film having a uniaxially oriented pore structure in this manner was immersed in ethanol to make an attempt to extract at 70°C for 24 hours. As a result, 90% or more of the surfactant was removed from the synthesized silica meso-structure by one extraction. In the case of a sample treated twice by the same extraction operations, 95% or more of the surfactant could be removed. A substrate formed with the pattern of a meso-porous silica thin film having a uniaxially oriented pore structure could be obtained by drying the thin film extracted finally to remove ethanol in the above step. It was confirmed from X-ray diffraction analysis that the mesoscopic pore structure was retained after the surfactant was

removed by extraction.

[0061] The method used to remove surfactant micelles by solvent extraction in this example is effective as a method for removing a surfactant from a silica meso-complex thin film formed on a substrate made of a resin or the like which is less resistant to heat treatment in an acidic atmosphere, though it is difficult to remove the surfactant perfectly. Also, this method of removing a surfactant by solvent extraction has the effect of keeping a higher level of the amount of a silanol group in the meso-porous silica thin film obtained finally as compared with the method using baking.

[0062] Example 3

This example is an example in which gold is used as the metal having acid resistance to form a pattern of a meso-porous silica thin film having a uniaxially oriented pore structure on a substrate.

[0063] The same gold pattern as that was shown in Fig. 4 was formed on a quartz glass substrate by using the photolithographic method. The film thickness of gold was about 100 nm. This substrate was washed with acetone, isopropyl alcohol and pure water to clean the surface in an ozone generator. Then, the same NMP solution of a polyamic acid A that was used in Examples 1 and 2 was applied to the substrate by spin coating and baked at 200°C for one hour to form a thin film of polyimide A.

[0064] The thin film was rubbed in one direction over the entire surface of the substrate in the same procedures as in Example 1 or 2 mentioned above and the obtained substrate was used as

a substrate for precipitating a silica meso-structure thin film having a uniaxially oriented pore structure.

[0065] Next, a silica meso-structure thin film was precipitated on this substrate in the same procedures as in Example 1 or 2 as mentioned above, followed by washing with pure water and ultrasonic treatment in pure water. Like the case of the gold pattern, the thin film formed on the place where gold was formed was perfectly peeled off and a transparent silica meso-structure thin film having a uniaxially oriented pore structure was formed on the part from which the quartz glass was exposed among the produced gold thin film pattern.

[0066] The substrate with the silica meso-structure thin film pattern which was formed in this manner was immersed in a gold etching solution prepared using 1.2 g of iodine, 8 g of ammonium iodide, 40 ml of water and 60 ml of methanol and held in the solution until gold was completely dissolved. The substrate formed with the pattern of the silica meso-structure after gold was removed by etching was fundamentally the same as that produced using a platinum thin film in Example 2. It was confirmed, from the X-ray diffraction analysis of the substrate obtained after gold was removed, that the treatment using the gold etching solution had no influence on the pore structure.

[0067] The substrate formed with the pattern of a silica meso-structure thin film having a uniaxially oriented pore structure in this manner was placed in a muffle furnace to heat the substrate up to 550°C at a rate of 1°C/min., followed by baking in the air for 10 hours. No large difference was observed

in the shape of the silica meso-structure thin film before and after the baking. Further, the X-ray diffraction analysis of the substrate with the silica meso-structure formed thereon after the baking was made, with the result that a diffraction peak with a plane spacing of 3.44 nm was observed to confirm that the hexagonal pore structure was retained.

[0068]

[Effect of the Invention] According to the present invention, as is explained above, a substrate is used which is prepared by forming a high-molecular compound thin film on a pattern of an acid-resistant metal thin film formed in advance and followed by rubbing treatment, which produces such an effect that a silica meso-structure thin film having a uniaxially oriented pore structure and precipitated on the metal thin film can be selectively peeled off and finally, a pattern of a silica meso-structure thin film or a meso-porous silica thin film having a desired shape and a uniaxially oriented pore structure can be finally formed at a desired position of the substrate.

[Brief Description of the Drawings]

[Fig. 1] Fig. 1 is a typical view for explaining a pattern of a silica meso-structure thin film having a uniaxially oriented pore structure according to the present invention which pattern is formed in Example 1 and for explaining the pore structure in the film.

[Fig. 2] Fig. 2 is a schematic view showing a reactor for forming a silica meso-complex thin film in the present invention.

[Fig. 3] Fig. 3 is an explanatory view showing a method for

holding a substrate in a reaction solution.

[Fig. 4] Fig. 4 is a schematic view showing a pattern of a platinum thin film formed on a quartz substrate which is used in Example 1 of the present invention.

[Fig. 5] Fig. 5 is a typical view of an optical microscopic image of a silica meso-structure thin film having a uniaxially oriented pore structure which film is formed by patterning in Example 1 of the present invention.

[Fig. 6] Fig. 6 is a typical view of a pattern of a silica meso-structure having a uniaxially oriented pore structure after a metal thin film is removed which pattern is formed in Example 2 of the present invention.

[Explanations of the Symbols]

11: Silica meso-structure having a uniaxially oriented pore structure

12: Platinum thin film

13: Quartz substrate

14: Polyimide orientation film treated by rubbing

15: Surfactant rod-like micelles or voids

16: Silica

21: Container (Teflon)

22: Lid (Teflon)

23: Substrate holder (made of Teflon)

24: Seal (O-ring)

25: Substrate

31: Reaction solution

32: Substrate

33: Spacer

34: Cover

41: Platinum thin film

42: Exposed part of a quartz substrate

51: Silica meso-structure having a uniaxially oriented pore structure

52: Texture

61: Silica meso-structure having a uniaxially oriented pore structure

62: Substrate

Fig. 1

Rubbing direction

Section

11 Silica meso structure

12 Platinum thin film

13 Quartz substrate

14 Polyimide orientation film

15 Surfactant rod-like micelles or voids

16 Silica

Fig. 2

21 Container

22 Lid

23 Substrate holder

24 Seal (O-ring)

25 Substrate

Fig. 3

31 Reaction solution

32 Substrate

33 Spacer

34 Cover

Fig. 4

Rubbing direction

41 Platinum thin film

42 Exposed part of a quartz substrate

Fig. 5

Rubbing direction

51 Silica meso-structure

52 Texture

Fig. 6

61 Silica meso-structure

62 Substrate